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DESCRIPTION

WATER-DEVELOPABLE PHOTOPOLYMER PLATE

FOR LETTERPRESS PRINTING

TECHNICAL FIELD

[0001]

The present invention relates to a water-  
developable photopolymer plate for letterpress printing  
5 and a method for producing the same.

BACKGROUND ART

[0002]

A commonly used photopolymer plate for  
letterpress printing is produced, for example, as  
10 described in Patent Documents 1 to 3, through an  
exposure step, a development step and a post-exposure  
step.

A printing method using a photopolymer plate  
for flexographic printing is a method in which an ink  
15 is supplied by using an ink supply roll or the like  
onto the surface of the raised areas of a polymer plate  
having raised and recessed areas and then, the polymer  
plate is brought into contact with a printing substrate  
so that the ink on the surface of the raised areas can  
20 be transferred onto the printing substrate. In such a  
flexographic printing, frequently in long-term  
printing, the ink sticks to the shoulders of the raised

areas of the photopolymer plate, or gets into the recessed areas in the polymer plate (hereinafter, referred to as plate surface staining). Consequently, the portions other than the true images are sometimes  
5 printed erroneously. In such cases, it is necessary that printing is once halted, and the surface of the polymer plate is wiped away with a strip of cloth by using a washing liquid such as alcohol, which is economically disadvantageous.

10 [0003]

On the other hand, the development of conventional photopolymer plates for letterpress printing generally adopts methods using organic solvents; however, from the viewpoint of environmental  
15 protection, plates permitting the use of aqueous developers are actively being developed. Techniques using such aqueous developers are proposed, for example, in Patent Documents 4 to 7 and the like. In water-developable photopolymer plates, there are used  
20 highly polar oligomers or monomers for liquid resins in order to impart water developability thereto. For solid resins, generally adopted is a technique in which a polar group-containing polymer is introduced as a polymer to constitute the main composition component,  
25 or a technique in which a polar group-containing polymer and a hydrophobic polymer are mixed and dispersed to be used. In particular, the latter method is preferably adopted because it leads to a better

plate durability and permits forming a high-definition plate surface.

[0004]

As a result of such composition

5 characteristics, a water-developable photopolymer plate for letterpress printing is more increased in the polarity of the plate surface as compared to a solvent-developable photopolymer plate containing as the main component a hydrophobic polymer such as a thermoplastic

10 elastomer, and hence is excessively increased in the affinity to the ink. Consequently, such an aforementioned phenomenon that the ink sticks to the shoulders of the raised areas, or gets into the raised areas in the polymer plate tends to occur more

15 frequently.

[0005]

In these years, the application of the letterpress printing to the high-definition printing has been promoted, and printing is made using halftone

20 dots in order to develop the gradation in color and density. In such printing, excessive ink causes the ink fill-in around the relief of fine halftone dots used in a halftone printing with a large number of halftone lines, namely, the bridging between dots.

25 Consequently, it causes marked degradation of printing quality to practically inhibiting the use of such halftone printing. Printing on plastic films has actively been carried out by using the letterpress

printing. However, when printing substrates altered from the paper substrates to plastic film substrates low in ink absorbability, a conventional water-developable photopolymer plate for letterpress printing suffers from the following drawback: poor ink transferability results exclusively in low-density solid quality and in blurred printing; and attempt to compensate the poor ink transferability by increasing the printing pressure results in a slight increase in the solid printed portion density but, in return for it, in significant defects such as thick lines and dots, to inhibit a well-balanced printing.

[0006]

Thus, conventional water-developable photopolymer plates for letterpress printing are limited in printable patterns and printing substrates because of the properties thereof in relation to the ink. Consequently, as affairs now stand, water-developable photopolymer plates for letterpress printing are limited in use in spite of the adaptability thereof to the environment.

[0007]

Thus, as for the plate surface staining of a polymer plate, various methods have been proposed.

Patent Document 8 describes a technique in which an organic fluorine compound is adhered onto the surface of a plate by brush coating or spraying. However, this is effective only in halftone dot

printing with a low number of lines and is insufficient in sustained effects, thus manifesting itself to be a method far away from solving the above described problems.

5 [0008]

Patent Document 9 describes a method in which a material selected from a silane coupling agent, a silicone oil and a silicone grease is internally added in a photopolymer, and then such a material is made to  
10 migrate to the surface of the photopolymer. This method is a method aiming at prevention of generation of tear flaws in plate making operation and the like, and a method in which a silicone compound is basically made to bleed. Accordingly, the silicone compound is  
15 removed from the surface at the time of printing, so that the sustainability of the hydrophobic effect of the surface due to silicone cannot be expected at all.  
[0009]

Patent Document 10 proposes a method in which  
20 a mixture composed of an aqueous emulsion including a silicone compound or a fluorine compound and an aqueous resin is coated. However, the coating of an aqueous solution having a low penetrating ability does not necessarily provide a sufficient effect of preventing  
25 the plate surface staining. Such an effect can hardly be sustained particularly in a long run printing or a repeated printing, which necessitates repetition of such a coating in order to maintain the effect.

[0010]

Patent Document 11 proposes a method in which the contact angle of the surface of the plate is made large by internally adding a hydrophobic compound, containing fluorine, chlorine or silicon, copolymerizable with the polymer material in a water-developable composition. This method is excellent in that such copolymerization with the photopolymer component makes it possible to fix the hydrophobization of the plate surface to the resin. However, as mentioned in the specification, applicable resins are restricted to liquid or paste-like homogeneous resins such as polyurethane resins, polyvinyl alcohol resins, polyester resins or nylon resins. The present inventors have revealed that unexpected adverse effects may occur when such a technique is applied to a resin system, among water-developable photopolymers, in which a polar group-containing polymer and a hydrophobic polymer are mixed and dispersed, and which provides a plate with durability and allows forming a high-definition plate surface. The adverse effects are such that when a fluorine compound or a silicone compound is being added to the resin system in which a polar group-containing polymer and a hydrophobic polymer are mixed and dispersed, the fluorine compound or the silicone compound results in bleeding from the resin, or the plate becomes turbid to cause light scattering at the

time of exposure, and consequently, image formation quality is degraded in such a way that there are caused, for example, failure in formation of fine lines and failure in shape of dots. Such addition of the hydrophobic compound as allowing suppressing to the utmost the degradation of image formation quality makes in turn the hydrophobic effect in the plate surface too small to attain the purpose. The operating mechanism to cause the turbid plate is not clear at present; however, it is inferred that the turbid plate may be ascribable to the light scattering amplified at the interface between the polar group-containing polymer and the hydrophobic polymer in which interface the hydrophobic substance tends to be present in the resin system wherein the polar group-containing polymer and the hydrophobic polymer are mixed and dispersed.

Patent Document 1: JP-A-10-171111

Patent Document 2: JP-A-63-088555

Patent Document 3: JP-A-05-134410

Patent Document 4: Japanese Patent No. 3508788

Patent Document 5: JP-B-58-33884

Patent Document 6: Japanese Patent No. 2940006

Patent Document 7: Japanese Patent No. 2985655

Patent Document 8: JP-A-51-40206

Patent Document 9: JP-A-60-191238

Patent Document 10: JP-A-2002-292985

Patent Document 11: JP-A-6-186740

## DISCLOSURE OF THE INVENTION

## PROBLEMS TO BE SOLVED BY THE INVENTION

[0011]

The problem of the present invention is to  
5 provide a method for producing a photopolymer plate  
wherein a water-developable photopolymer plate for  
letterpress printing is adopted, the photopolymer plate  
is capable of printing with a satisfactory balance  
between the high definition and the high density in the  
10 solid printed portions without degrading the image  
formability thereof, the ink blot of the plate surface  
can be prevented over a long period of time, and the  
photopolymer plate can be spared, to the highest  
possible degree, from cumbersome operations such as  
15 plate wiping in the printing process.

## MEANS FOR SOLVING THE PROBLEMS

[0012]

For the purpose of solving the aforementioned  
problems, the present inventors have made a diligent  
20 study. Consequently, the present inventors have  
completed the present invention by discovering that the  
problems can be solved by bringing the surface of the  
polymer plate, during or after an exposure step, into  
contact with a liquid containing a silicone compound  
25 and/or a fluorine compound.

[0013]

More specifically, the present invention may



be described as follows.

(1) A method for producing a water-developable photopolymer plate for letterpress printing comprising an exposure step, a development step and a post-  
5 exposure step, wherein the photopolymer plate is brought into contact with a liquid comprising a modified silicone compound and/or a modified fluorine compound during or after the exposure step.

(2) The method according to (1), wherein the  
10 photopolymer comprises: a binder polymer comprising a polar group-containing polymer and a hydrophobic polymer; an ethylenically unsaturated compound; and a photopolymerization initiator.

(3) The method according to (1) or (2), wherein  
15 the modified silicone compound and/or the modified fluorine compound comprises one or more modifying groups selected from the group consisting of a hydroxy group, a carbinol group, an epoxy group, a (meth)acrylate group, a carboxyl group, a carboxylate  
20 group, an amino group, an aromatic hydrocarbon group inclusive of a phenyl group, a hydrocarbon group substituted with an aromatic hydrocarbon inclusive of a methylstyryl group, an aromatic hydrocarbon group substituted with a hydroxy group inclusive of a  
25 hydroxyphenyl group, an alkoxyl group, a (poly)ether group and a urethane group.

(4) The method according to any one of (1) to (3), wherein an irradiation with actinic light is

carried out after the photopolymer plate has been brought into contact with the liquid comprising the modified silicone compound and/or the modified fluorine compound.

- 5 (5) The method according to (4), wherein the photopolymer plate is brought into contact with the liquid comprising the modified silicone compound and/or the modified fluorine compound after the development step and immediately before the post-exposure step.
- 10 (6) The method according to (4) or (5), wherein development is carried out by using a developer comprising the modified silicone compound and/or the modified fluorine compound.
- (7) The method according to (6), wherein the  
15 modified silicone compound is a silicone compound comprising one or more modifying groups selected from the group consisting of a hydroxy group, a carbinol group, an epoxy group, a (meth)acrylate group, a carboxyl group, a carboxylate group, an amino group and  
20 a (poly)ether group.
- (8) The method according to any one of (1) to (3), wherein the post-exposure step is carried out while the photopolymer plate is being brought into contact with the liquid comprising the modified  
25 silicone compound and/or the modified fluorine compound.
- (9) The method according to (1), wherein the liquid comprising the modified silicone compound and/or

the modified fluorine compound is a developer.

(10) A developer, comprising a modified silicone compound and/or a modified fluorine compound, for use in producing a water-developable photopolymer plate for letterpress printing.

(11) The developer according to (10), comprising:  
(a) 1 to 50 parts by weight of one or more surfactants;  
(b) 0.01 to 20 parts by weight of the modified silicone compound; (c) 0.2 to 20 parts by weight of an alkyl glycol ether; and (d) 0.1 to 10 parts by weight of an alkali builder.

(12) The developer according to (10) or (11), wherein the modified silicone compound is a silicone compound comprising one or more modifying groups selected from the group consisting of a hydroxy group, a carbinol group, an epoxy group, a (meth)acrylate group, a carboxyl group, a carboxylate group, an amino group and a (poly)ether group.

(13) A water-developable photopolymer plate for letterpress printing produced by the method according to any one of (1) to (9).

(14) A water-developable photopolymer plate for letterpress printing, comprising silicon on a surface thereof in a relative element concentration of 0.1 at% or more.

(15) The water-developable photopolymer plate for letterpress printing according to (13) or (14), wherein a rate of a change of a diameter of an indicator of

surface wettability between before and after a treatment by using a 20/80 (weight ratio) ethyl acetate/isopropyl alcohol mixed solvent is 25% or less.

(16) The water-developable photopolymer plate for  
5 letterpress printing according to (13) or (14),  
comprising silicon on the surface of the polymer in a relative element concentration of 0.1 at% or more after the treatment by using the 20/80 (weight ratio) ethyl acetate/isopropyl alcohol mixed solvent.

#### 10 ADVANTAGES OF THE INVENTION

[0014]

According to the production method of the present invention, there can be provided a water-developable photopolymer plate for letterpress printing  
15 wherein the photopolymer plate is capable of printing with a satisfactory balance between the high definition and the high density in the solid printed portions without degrading the image formability thereof, the ink blot of the plate surface can be prevented over a  
20 long period of time, and the photopolymer plate can be spared, to the highest possible degree, from cumbersome operations such as plate wiping in the printing process.

#### BEST MODE FOR CARRYING OUT THE INVENTION

25 [0015]

The present invention will be described below

in detail, particularly with a focus on the preferred embodiments.

A water-developable photopolymer plate for letterpress printing of the present invention is  
5 produced through an exposure step, a development step and a post-exposure step. The resin prior to exposure may be fluid or solid at room temperature, and usually, the plate thickness of a usually used plate falls within a range from 0.5 to 10 mm. There may be used a  
10 resin well known in the art as used in a water-developable photopolymer plate. Examples of such a resin may include, for example, those resins proposed in Patent Documents 4, 5, 6 and 7, and the like. A fundamental constitution of such a resin comprises an  
15 oligomer or polymer component, a polymerizable monomer component, a photoinitiator and a stabilizer. A variety of materials can be used as the oligomer or polymer component that has the most significant effect on the physical properties of the plate; examples of  
20 the cases using such materials include various cases in each of which there is used a polyurethane resin, a polyvinyl alcohol resin, a polyester resin, a nylon resin or a resin (binder polymer) in which a polar group-containing polymer and a hydrophobic polymer are  
25 mixed and dispersed. In particular, when there is used a resin in which a polar group-containing polymer and a hydrophobic polymer are mixed and dispersed, the durability and the high definition plate surface

formability of the plate are excellent, and such a resin is high in general versatility and useful in printing. Examples of such a resin may include the following.

5 [0016]

Examples of a polar group-containing polymer may include water soluble or water dispersible copolymers each of which contains a hydrophilic group such as a carboxyl group, an amino group, a hydroxy  
10 group, a phosphoric acid group or a sulfonic acid group, or a salt of such a group. More specifically, examples of a polar group-containing polymer may include: a carboxyl group-containing NBR and a carboxyl group-containing SBR described in Japanese Patent No.  
15 2128098; carboxyl group-containing polymers of aliphatic conjugated dienes described in JP-A-5-7705, JP-A-61-128243, JP-A-6-194837, JP-A-7-134411 and the like; a phosphoric acid group-containing or carboxyl group-containing emulsified polymer of an ethylenically  
20 unsaturated compound described in JP-A-9-15860; a sulfonic acid group-containing polyurethane described in JP-A-3-206456; and a carboxyl group-containing butadiene latex described in Japanese Patent Application No. 2000-361371. These hydrophilic  
25 polymers may be used each alone or in combinations of two or more thereof.

[0017]

The hydrophobic polymers to be used in

combination with these hydrophilic polymers may be polymers obtained by polymerizing conjugated diene hydrocarbons and copolymers obtained by polymerizing a conjugated diene hydrocarbon and a monoolefin

5 unsaturated compound; examples of such hydrophobic polymers may include: a butadiene polymer, an isoprene polymer, a chloroprene polymer, a styrene-butadiene copolymer, a styrene-butadiene-styrene copolymer, a styrene-isoprene copolymer, a styrene-isoprene-styrene  
10 copolymer, a styrene-chloroprene copolymer, an acrylonitrile-butadiene copolymer, an acrylonitrile-isoprene copolymer, a methyl methacrylate-butadiene copolymer, a methyl methacrylate-isoprene copolymer, an acrylonitrile-butadiene-styrene copolymer, and an  
15 acrylonitrile-isoprene-styrene copolymer. These hydrophobic polymers may be used each alone or in combinations of two or more thereof.

[0018]

No particular constraint is imposed on the  
20 polymerizable monomers to be used in combinations with these oligomer or polymer components. Examples of such a monomer may include ester compounds between ethylenically unsaturated acids and alcohols, and those compounds described in a reference "Photocuring  
25 Technique Data Book (Hikari Koka-gijutu Data Book) (published by Technonet Co., Ltd.)" and the like. More specifically, examples of such monomers may include: straight chain, branched and cyclic monofunctional

monomers such as hexyl (meth)acrylate, nonane (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, 2-ethyl, 2-butylpropanediol (meth)acrylate, hydroxyethyl (meth)acrylate, 2-

5 (meth)acryloyloxyethyl hexahydrophthalate, 2- (meth)acryloyloxyethyl phthalate, (meth)acrylic acid dimer, ECH-modified allyl acrylate, benzyl acrylate, caprolactone (meth)acrylate, dicyclopentenyl (meth)acrylate, isobornyl (meth)acrylate and cyclohexyl

10 (meth)acrylate; and straight chain, branched and cyclic multifunctional monomers such as hexanediol di(meth)acrylate, nonanediol di(meth)acrylate, 2-ethyl, 2-butylpropane di(meth)acrylate, neopentylglycol di(meth)acrylate, neopentylglycol hydroxypivalate

15 di(meth)acrylate, ECH-modified phthalic acid di(meth)acrylate, tricyclodecane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ECH-modified glycerol tri(meth)acrylate, trimethylolpropane benzoate

20 (meth)acrylate, EO(PO)-modified trimethylolpropane tri(meth)acrylate and dipentaerythritol hexa(meth)acrylate. Alternatively, examples of such monomers may include esters between alcohols and fumaric acid such as dioctyl fumarate, and N-

25 substituted maleimide derivatives such as laurylmaleimide and cyclohexylmaleimide.

[0019]

Examples of the photopolymerization initiator



used as one of the other components may include those described in references, "Photocuring Technique Data Book (Hikari Koka-gijutu Deta Bukku) (published by Technonet Co., Ltd.), "Ultraviolet Curing System 5 (Shigaisen Koka Shisutemu) (published by Sogo Gijutsu Center) and the like. More specifically, examples of the photopolymerization initiator may include benzophenone, Michler's ketone, benzoin, benzoin methyl ether, benzoin ethyl ether,  $\alpha$ -methylolbenzoin,  $\alpha$ -10 methylolbenzoin methyl ether, benzyl methyl ketal, 1-hydroxy-cyclohexyl-phenyl ketone, benzophenone, acrylated benzophenone, methyl o-benzoylbenzoate, bisacyl phosphine oxide,  $\alpha$ -methoxybenzoin methyl ether, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-15 phenylacetophenone, 2-methyl-1-(4-methylthio)phenyl, 2-morpholinopropan-1-one, thioxanthone, benzil and anthraquinone. These may be used each alone or in combinations of two or more thereof.

[0020]

20                    Additionally, there may be blended, if needed, additives such as a polymerization inhibitor, a plasticizer, a dye, an ultraviolet absorber and an antiozonant. Examples of the plasticizer may include liquid 1,2(or 1,4)-polybutadiene, 1,2(or 1,4)-25 polyisoprene, and terminal modified products of these compounds; and hydrocarbon oils such as naphthene oil and paraffin oils. Examples of the polymerization inhibitor may include phenols such as hydroquinone, p-

methoxyphenol, 2,4-di-t-butylcresol, catechol and t-butylcatechol.

[0021]

In the case of a solid photopolymer, usually  
5 a plate is formed by using a polyethylene terephthalate support (a support imparted with antihalation effect is used if needed) and a film having an adhesion preventing layer. In the case of a digital plate referred to as flexo-CTP, a plate is formed by using  
10 the aforementioned support and a film having a laser ablation layer. In the case of a liquid photopolymer, the resin is inserted between a support and a film on a commercially available platemaker for a liquid photopolymer, and then subjected to exposure.

15 [0022]

Usually, a water-developable photopolymer plate is produced by applying an exposure step (an exposure step with actinic light) and a development step (a washing-out step of the unexposed portions),  
20 and then a post-exposure step. In the present invention, it is necessary to bring the photopolymer plate, during or after the exposure step, into contact with a liquid containing a silicone compound and/or a fluorine compound. The silicone compound as referred  
25 to herein means an oligomer or polymer the skeleton of which is mainly formed with an alkylsiloxane having an alkyl group typified by a methyl group, and a substance sometimes generally referred to as a silicone oil or

the like. The fluorine compound as referred to herein means a compound in which the hydrogen atoms of a hydrocarbon compound are partially or completely substituted with fluorine atoms.

5 [0023]

The silicone compound and/or the fluorine compound to be used in the present invention preferably contains a functional group having interaction and/or reactivity with the resin component. More  
10 specifically, preferable examples of such a functional group may include functional groups such as a hydroxy group, a carbinol group, an epoxy group, a (meth)acrylate group, a carboxyl group, a carboxylate group, an amino group, an aromatic hydrocarbon group  
15 inclusive of a phenyl group, a hydrocarbon group substituted with an aromatic hydrocarbon inclusive of a methylstyryl group, an aromatic hydrocarbon group substituted with a hydroxy group inclusive of a hydroxyphenyl group, an alkoxyl group, a (poly)ether  
20 group and a urethane group. A silicone compound and/or a fluorine compound each containing one or more such modifying groups is referred to as a modified silicone compound and/or a modified fluorine compound. In such a modified silicone compound and/or such a modified  
25 fluorine compound, the aforementioned one or more modifying groups may be directly bonded to a Si atom (Si atoms) and/or a F atom (F atoms), or may replace one or more hydrogen atoms of a hydrocarbon group

bonded to a Si atom and/or a F atom.

[0024]

The investigation of the present inventors has revealed that even if the photopolymer plate is brought into contact with a silicone compound having no modifying group, for example, a silicone oil the main chain of which is formed with dimethylsiloxane, and/or a fluorine compound having no modifying group, for example, a fluorine oil such as a perfluorocarbon, a hydrofluoroether or a hydrofluorocarbon, no hydrophobilization effect of the surface of the photopolymer plate is attained, or such effect is lost at the initial stage of printing. It can be inferred that this phenomenon is ascribable to the unsuccessful fixation of these compounds to the surface of the photopolymer plate owing to the poor penetration of these compounds into the photopolymer plate, or the poor intermolecular interaction or reactivity with the photopolymer plate.

[0025]

No constraint is imposed on the method for bringing the photopolymer plate into contact with the modified silicone compound and/or the modified fluorine compound. For example, a treatment liquid is prepared in advance by dissolving such a compound or such compounds in an organic solvent, or an alcohol, preferably an alcohol having 1 to 6 carbon atoms, more preferably ethanol, methanol or isopropyl alcohol.

Then, at an appropriate time after the exposure step, the plate can be soaked in the treatment liquid, or the treatment liquid can be coated on the surface of the plate by means of an atomizer, a brush, or the like.

5 When such a treatment liquid is used, the concentration of the silicone compound and/or the fluorine compound in the treatment liquid usually falls within a range from 0.001% by weight to 50% by weight, preferably from 0.01% by weight to 20% by weight, and more preferably  
10 from 0.1% by weight to 10% by weight or less. When the concentration is lower than these ranges, no sufficient hydrophobilization effect can be attained. When the concentration exceeds these ranges, the cost for treatment is unpreferably increased without any  
15 increased advantageous effect. If needed, the solution containing the silicone compound and/or the fluorine compound may be added with additives such as an antifoaming agent, an antioxidant or an antiseptic agent.

20 [0026]

Alternatively, the modified silicone compound and/or the modified fluorine compound is dissolved or dispersed in the developer to be used in the development step of the photopolymer, and the surface  
25 of the plate can be brought into contact with the modified silicone compound and/or the modified fluorine compound while the photopolymer plate having been subjected to the exposure step is being developed.

This method is a preferable embodiment from the viewpoint that this method can be implemented without further adding a step for bringing the surface of the plate into contact with the modified silicone compound and/or the modified fluorine compound.

[0027]

As the development method, any methods well known in the art may be adopted. Specifically, examples of such development methods may include a development method in which the unexposed portions are dissolved or scraped away with a brush while the plate is being soaked in a washing liquid; and another development method in which the unexposed portions are dissolved or scraped away with a brush while the plate surface is being sprinkled with a washing liquid by means of a spray. Developers known in the art can be used as the developer for the water-developable photopolymer plate. Such developers usually contain a surfactant as an effective component. Examples of such a surfactant may include an anionic surfactant, an amphoteric surfactant and a nonionic surfactant. These surfactants may be used each alone or as mixtures of two or more thereof.

[0028]

Examples of the anionic surfactant may include a sulfate salt, a higher alcohol sulfate, a higher alkyl ether sulfate, a sulfated olefin, an alkylbenzene sulfonate, an  $\alpha$ -olefin sulfonate, a

phosphate and a dithiophosphate. Examples of the amphoteric surfactant may include an amino acid-type amphoteric surfactant and a betaine-type amphoteric surfactant. Examples of the nonionic surfactant may  
5 include polyethylene glycol type surfactants such as a higher alcohol ethylene oxide adduct, an alkylphenol ethylene oxide adduct, a fatty acid ethylene oxide adduct, a polyhydric alcohol fatty acid ester ethylene oxide adduct, a higher alkylamine ethylene oxide  
10 adduct, a fatty acid amide ethylene oxide adduct and a polypropylene glycol ethylene oxide adduct; and polyhydric alcohol type surfactants such as a glycerol fatty acid ester, a pentaerythritol fatty acid ester, fatty acid esters of sorbitol and sorbitan, alkyl  
15 esters of polyhydric alcohols and fatty acid amides of alkanolamines.

[0029]

It is an effective method to add, in addition to these, a water-miscible organic solvent such as an  
20 alkylglycol ether as a penetrating agent, for the purpose of improving the washability of the plate and the penetration of the silicone compound into the plate. The penetrating agent can be selected according to the composition of the resin to be washed. Examples  
25 of such a penetrating agent may include mono or polyethylene glycol ether type nonionic penetrating agents such as dibutyl diglycol ether.

As additional components, a PH adjuster,

referred to as an alkali builder, may be added; the usable alkali builder may be an organic or inorganic material, and is preferably capable of adjusting the pH to be 9 or more. Examples of such an alkali builder  
5 may include sodium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate and sodium succinate.

[0030]

No particular constraint is imposed on the amounts of the surfactant, penetrating agent and  
10 builder in the developer. Usually, the amount of the surfactant, in relation to the weight of the developer, is 1 part by weight to 50 parts by weight, and more preferably 3 parts by weight to 20 parts by weight. The penetrating agent is usually used in a range from  
15 0.2 part by weight or more to 20 parts by weight or less, and more preferably from 0.2 part by weight or more to 10 parts by weight or less, in relation to the weight of the developer. The alkali builder is usually used in a range from 0.1 part by weight to 10 parts by  
20 weight, in relation to the weight of the developer.

When the amounts of these components are less than the above described ranges, there occur disadvantageous effects such that the time required for development becomes too long. The case in which the amounts of  
25 these components exceed the above described ranges is not preferable from the viewpoint of cost.

[0031]

As described above, the modified silicone



compound and/or the modified fluorine compound is dissolved or dispersed in the developer used in the development step of the photopolymer, and the surface of the plate can be brought into contact with the

5 modified silicone compound and/or the modified fluorine compound while the photopolymer plate having been subjected to the exposure step is being developed. When this method is applied, from the viewpoint of the stability of the dissolution or dispersion in the

10 developer, particularly preferable is the modified silicone compound and/or the modified fluorine compound each of which has one or more modifying groups selected from the group consisting of a hydroxy group, a carbinol group, an epoxy group, a (meth)acrylate group,

15 a carboxyl group, a carboxylate group, an amino group and a (poly)ether group. In such a modified silicone compound and/or such a modified fluorine compound, the aforementioned one or more modifying groups may be directly bonded to a Si atom (Si atoms) and/or a F atom

20 (F atoms), or may replace one or more hydrogen atoms of a hydrocarbon group bonded to a Si atom and/or a F atom. The concentration of the modified silicone compound and/or the modified fluorine compound in the developer is preferably 0.01 part by weight to 20 parts

25 by weight, and more preferably 0.1 part by weight to 5 parts by weight. When the concentration is lower than these ranges, no sufficient hydrophobilization effect can be attained. On the other hand, the concentration

exceeding these ranges unpreferably increases the cost for treatment without any increased advantageous effect, and sometimes causes adverse effects such that the development rate of the developer is decreased.

5           When two or more reagents are used in combination, the ratios between the reagents can be optional, but the total amount thereof preferably falls within the above describe ranges.

[0032]

10           In the method of the present invention, the effects of the modifying group(s) in the modified silicone compound and/or the modified fluorine compound make it possible to dispose the hydrophobicity-attaining silicone molecules and/or the hydrophobicity-attaining fluorine-containing molecules, each in a high  
15           concentration, on the surface of the photopolymer. Conceivably, these molecules are fixed to the surface through the interactions and/or reactions thereof with the components in the photopolymer, and consequently,  
20           various problems to occur in printing can be avoided effectively and sustainably. Accordingly, the types and amounts of the modifying groups in the modified silicone compound and/or the modified fluorine compound should be appropriately selected according to the type  
25           of the photopolymer to be used.

[0033]

          However, for example, when a solvent based ink exhibiting high penetration into the plate itself

is used for printing, sometimes a phenomenon of gradual degradation of the hydrophobilization effect is identified. The present inventors have found that, in such a case, the sustainability of the

5 hydrophobilization effect is improved by irradiation of actinic light after being brought into contact with the modified silicone compound and/or the modified fluorine compound. The actinic light as referred to herein means a light containing at least light of 300 nm or

10 less in wavelength. Actinic light containing light of 300 nm or more in wavelength may be used at the same time if needed. When two or more types of actinic light different in wavelength are irradiated, these types of light may be irradiated at the same time or at

15 separate times. Such irradiation of the plate may be made as an exposure treatment in the air, or may be carried out in a system from which oxygen is eliminated, namely, under a vacuum condition, in an atmosphere of nitrogen gas or another inert gas, in a

20 state in which the plate is immersed in water, or the like.

[0034]

The reason for the improvement effect of the sustainability of the hydrophobilization effect has not

25 yet been elucidated. Even after the photopolymer plate has been exposed, the photopolymerization initiator remains, and conceivably the irradiation of actinic light to the photopolymer plate generates reactive

species in the vicinity of the surface of the plate to cause bonding between the photopolymer component and the modified silicone compound and/or the modified fluorine compound. The irradiation of actinic light may be carried out after the exposure step, and at any time during or after the contact of the modified silicone compound and/or the modified fluorine compound with the photopolymer plate. Usually, the photopolymer plate is produced through the exposure, development and post-exposure steps. Accordingly, the photopolymer plate is brought into contact with the modified silicone compound and/or the modified fluorine compound after the development step and immediately before the post-exposure step, and then the post-exposure and the irradiation with actinic light may be carried out at the same time. For example, there may be adopted a method in which the post-exposure and the irradiation with actinic light are carried out at the same time under the condition such that the modified silicone compound and/or the modified fluorine compound is dispersed in water. Alternatively, the irradiation with actinic light may be carried out as an appropriate step in a manner separated from the post-exposure step. The irradiation should be carried out by appropriately selecting the type of the actinic light source and the irradiation light quantity so as to attain the desired effects properly.

[0035]

The present inventors have made a further detailed investigation on the advantageous effects of the photopolymer plate produced by bringing the photopolymer plate into contact with a liquid  
5 containing the modified silicone compound and/or the modified fluorine compound according to the method of the present invention. Consequently, there has been found a method in which, by measuring the change of the surface property of the photopolymer plate after  
10 soaking thereof in a solvent under specified conditions, the advantageous effects desired to be attained in practical printing by the photopolymer plate according to the present invention, in particular, the practical sustainability of the  
15 advantageous effects can be identified.

[0036]

The above mentioned method is a method in which the photopolymer plate is soaked at 20°C for 4 hours in a mixed solvent of ethyl acetate and isopropyl  
20 alcohol, in a weight ratio of 20 to 80, both to be used in the solvent ink; then the plate is further dried at 60°C for 4 hours or more; and the surface wettability of this photopolymer plate is compared with the surface wettability of the photopolymer plate before the  
25 application of the treatment concerned. The measurement method of the surface wettability as referred to herein is such that in an atmosphere at a room temperature of 20°C and a humidity of 70%, 0.5 ml

of a 30 dyne/cm wet tensile test standard solution to be used in the JIS K6768 test method is dropped onto the solid surface of the plate from a height of 20 mm, and the diameter of the solution droplet at 30 seconds after dropping is measured. The diameter of the solution droplet is an average value of the X and Y direction values, and each sample is measured three times, an average value of which is taken as the result. Between before and after the above described treatment using the mixed solvent of ethyl acetate and isopropyl alcohol, the diameter of the indicator tends to increase, namely, the hydrophobicity tends to decrease. However, it has been found that when the variation rate of the diameter is 25% or less, more preferably, 15% or less, a practical sustainability of the advantageous effect in practical printing can be attained. It has also been found that a similar result can be obtained even when this method is applied by using an ink having a high penetration into the plate such as an UV ink, in place of the mixed solvent of ethyl acetate and isopropyl alcohol. Accordingly, the following is also an aspect of the present invention: a water-developable photopolymer plate for letterpress printing for which the rate of the diameter variation of the surface wettability indicator between before and after the treatment, with the 20/80 (weight ratio) ethyl acetate/isopropyl alcohol mixed solvent, of the photopolymer plate having been brought into contact

with the modified silicone compound and/or the modified fluorine compound is 25% or less.

[0037]

Additionally, the present inventors have made  
5 a diligent study on the method for scientifically  
analyzing the surface of the treated photopolymer  
plate. Consequently, it has been found that  
particularly when the modified silicone compound is  
used, the following plate can attain a practical  
10 sustainability of the advantageous effect in practical  
printing: the photopolymer plate for which the relative  
element concentration of the silicon present on the  
surface of the photopolymer plate as measured by XPS is  
0.1 at% or more, and more preferably 0.5 at% or more,  
15 after the treatment with the mixed solvent of ethyl  
acetate and isopropyl alcohol. Here, it should be  
noted that "at%" refers to the ratio in terms of the  
number of atoms on the surface of the photopolymer  
plate (relative element concentration). The following  
20 is also an aspect of the present invention: a water-  
developable photopolymer plate for which, after the  
treatment with the mixed solvent of ethyl acetate and  
isopropyl alcohol, the silicon concentration on the  
surface of the photopolymer plate having been brought  
25 into contact with the modified silicone compound is 0.1  
at% or more.

[0038]

In the resin of the water-developable

photopolymer plate for letterpress printing to be used in the present invention, there may be internally added the modified silicone compound and/or the modified fluorine compound to be used, in the method of the present invention, for bringing the photopolymer plate into contact therewith during or after the exposure step for the photopolymer plate. However, such internal addition should be carried out as long as there occur no such adverse effects that the photopolymer plate becomes turbid to cause light scattering when exposed, and consequently, image formation quality is degraded in such a way that there are caused, for example, failure in formation of fine lines and failure in shape of dots. The advantage of such internal addition may include a case where there can be expected an advantageous effect such that the slidability of the photopolymer plate is improved in printing on coarse surface paper or the like to suppress the wear-out of the photopolymer plate, and thus such internal addition can be made if needed. Such a method for bringing the photopolymer plate into contact with the modified silicone compound and/or the modified fluorine compound during or after the exposure step is also an embodiment of the present invention.

25 [0039]

Hereinafter, the present invention will be described more specifically with reference to Examples and Comparative Examples, but the present invention is



not limited these.

[Synthesis Example]

<Synthesis of hydrophilic copolymer A>

In a pressure reaction vessel equipped with a stirrer and a temperature control jacket, 125 parts by weight of water and 3 parts by weight of an emulsifying agent (the ammonium salt of  $\alpha$ -sulfo(1-(nonylphenoxy)methyl-2-(2-propenyloxy)ethoxy-poly(oxy-1,2-ethanediyl)) (trade name: ADEKA REASOAP, manufactured by ASAHI DENKA Co., Ltd.)) were initially placed. The internal temperature was elevated up to a polymerization temperature of 80°C; then, an oily mixed solution composed of 2 parts by weight of acrylic acid, 5 parts by weight of methacrylic acid, 60 parts by weight of butadiene, 10 parts by weight of styrene, 23 parts by weight of butyl acrylate and t-dodecylmercaptane, and an aqueous solution composed of 28 parts by weight of water, 1.2 parts by weight of sodium peroxodisulfate and 1 part by weight of an emulsifying agent (trade name: ADEKA REASOAP, manufactured by ASAHI DENKA Co., Ltd.) were added thereto over a period of 5 hours and a period of 6 hours, respectively, each at a constant flow rate. The reaction liquid thus obtained was maintained at the same temperature as above for 1 hour to complete the polymerization, and subsequently the reaction liquid was cooled. Then, the produced latex was adjusted to pH7 with sodium hydroxide, thereafter the unreacted

substances were removed by steam stripping, and finally, an aqueous solution of a hydrophilic polymer having a the solid content concentration of 40% was obtained, which was dried at 60°C to yield the

5 hydrophilic copolymer A.

[0040]

[Evaluation of ink fill-in]

The ink fill-in was evaluated by means of an AI-3 type flexographic press (manufactured by IYO KIKAI

10 SEISAKUSYO Co., Ltd.) and a 600LPI (volume:  $3.8 \text{ cm}^3/\text{m}^2$ ) anilox roll. The ink used was an aqueous ink "HW571AQP Process Cyan" (trade name; manufactured by TOYO INK MFG CO., LTD.) that was adjusted to have a viscosity of 15 seconds (Zhan viscometer #4). The used printing

15 substrate was a coated paper (trade name: Pearl Coat; manufactured by Oji Paper Co., Ltd.; basic weight:  $106 \text{ g}/\text{m}^2$ ). The adopted printing speed was 100 m/min. The anilox pressure was set at a value larger by 0.02 mm than the proper value in order to supply the ink

20 excessively onto the photopolymer plate for the purpose of accelerating the ink fill-in. Also for the same purpose, the printing pressure condition was such that the printing pressure was set at a value larger by 0.15 mm than the proper value so that the deformation of the

25 relief surface could be made larger to accelerate the ink full-in. After a 100 m printing had been made under the above described printing conditions, the anilox roll was separated away from the photopolymer

plate. Then, a 10 m printing was made under a condition that the photopolymer plate was away from the anilox roll to remove the excessive ink from the surface of the photopolymer plate. Then, the printing press was halted, and the evaluation was made on the basis of the degree of the ink remaining in the halftone dot portions of the plate. In the image for evaluation, there were 16 halftone dots each of which was designed to have one of the line densities of 100, 133, 150 and 175 LPI and also to have one of the line-drawn area ratios of 1, 2, 3 and 5%. The evaluation was made on the basis of the number of the halftone dots in each of which 30% or more of the image area was found to suffer ink fill-in. In a preferable plate material that hardly suffers ink fill-in, the degree of ink fill-in is expected to be low, with the highest possible evaluation number of 0. On the other hand, in a plate material liable to suffer ink fill-in, the number of the halftone dots suffering ink fill-in is inevitably increased, with the largest possible number of 16.

[0041]

[Evaluation of the surface wettability of the photopolymer plate]

The evaluation of the surface wettability of the photopolymer plate was carried out on the basis of the following method. In an atmosphere at a room temperature of 20°C and a humidity of 70%, 0.5 ml of a

30 dyne/cm wet tensile test mixed solution No. 30.0  
(manufactured by Wako Pure Chemical Industries, Ltd.)  
was dropped from a height of 20 mm onto the solid  
surface of the plate, and the diameter (unit: mm) of  
5 the solution droplet at 30 seconds after dropping was  
measured. The diameter of the solution droplet was an  
average value of the X and Y direction values, and each  
sample was measured three times, an average value of  
which is taken as the result. On a photopolymer plate  
10 liable to suffer ink fill-in, namely, a photopolymer  
plate having a better wettability, the solution droplet  
is expanded so as to have a larger diameter; on the  
contrary, on a plate to hardly suffer ink fill-in,  
namely, a plate having a worse wettability, the  
15 solution droplet is hardly expanded so as to have a  
smaller diameter; thus, the measurement of the solution  
droplet diameter enables a comparison of wettability.  
[0042]

[Evaluation of the sustainability of the treatment  
20 effect]

The sustainability of the treatment effect as  
referred to herein refers to the durability in relation  
to the solvent and the UV ink, as described below, and  
the evaluation of the surface wettability of the  
25 individual photopolymer plates was carried out  
according to the above described method.

Evaluation example 1: Treatment effect test  
for resistance to solvent (Soaking test 1)

A prepared photopolymer plate was soaked in the 20/80 (weight ratio) ethyl acetate/isopropyl alcohol mixed solvent at 20°C for 4 hours, and the surface wettability of the photopolymer plate was  
5 evaluated after drying at 60°C for 4 hours or more.

Evaluation example 2: Treatment effect test for resistance to UV ink (Soaking test 2)

A prepared photopolymer plate was soaked in a flexo UV ink "UFL639 indigo" (manufactured by The  
10 Incteck Inc.) at 20°C for 4 hours, and then the ink was washed with isopropyl alcohol. The photopolymer plate was dried at 60°C for 4 hours, and the surface wettability of the photopolymer plate was evaluated.  
[0043]

15 [Measurement of the Si concentration]

The relative element concentration of the silicon present on the surface of a photopolymer plate was measured by means of XPS. The measurement conditions were as described below.

20 Apparatus: ESCALAB250 manufactured by Vacuum Generator

Excitation sources: Monochromated AlK $\alpha$ , 15 kV  
x 10 mA

Analysis area: An ellipse of 300  $\mu$ m x 600  $\mu$ m  
25 Scanning range  
Survey scan: 1,100 to 0 eV (for qualitative analysis)

Narrow scan: Cls, Ols, Si2p, S2p, Nals (for

quantitative analysis, chemical state analysis)

Pass energy

Survey scan: 100 eV

Narrow scan: 20 eV

5 In the quantitative determination, the relative element concentrations were calculated by using the area intensities of the Cls, Ols, Si2p, S2p and Nals together with the relative sensitivity coefficients, in terms of the unit of at%. The applied  
10 relative sensitivity coefficients were as follows:

Cls: 1.00; Ols: 2.72; Si2p: 0.93; S2p: 1.67;

Nals: 8.52

[0044]

[Evaluation in practical printing]

15 The used ink was a solvent-based ink FB King (indigo, manufactured by TOYO INK MFG CO., LTD.), and the used printing substrate was a low density polyethylene. A printing of 50,000 sheets was carried out at a speed of 200 m/min, by using an anilox roll of  
20 an 800 lpi (cell volume:  $3.8 \text{ cm}^3/\text{m}^2$ ) and a cushion tape of 3M1020 (manufactured by Sumitomo 3M Co., Ltd.). The photopolymer plates used for evaluation were designed with solid printed portions, independent dots and independent lines, void lines, and segments each having  
25 one of the screen rulings of 100, 133, 150 and 175 lpi, and also having one of the dot area ratio of 1, 2, 3 and 5%. The evaluation "C" refers to the case in which the halftone dot portion suffers ink fill-in before

completion of printing to lead to a state that printing is needed to be halted; the evaluation "B" refers to the case in which printing is completed, but the density in the solid printed portion decreases or the  
5 halftone dot portion becomes thick; and the evaluation "A" refers to the case in which printing is completed, and the density of the solid printed portion does not decrease and the halftone dot portion does not become thick.

10 [0045]

[Example 1]

A photopolymer composition was obtained by homogeneously kneading, with a kneader at 130°C, 30 parts by weight of the hydrophilic copolymer A  
15 described in the above synthesis example, 25 parts by weight of a styrene-butadiene-styrene block copolymer (KRATON KX405, Shell Chemical), 30 parts by weight of a liquid polybutadiene (LIR305, KURARAY Co., Ltd.), 2.5 parts by weight of hexamethylene dimethacrylate, 8  
20 parts by weight of 2-butyl, 2-ethylpropanediol diacrylate, 2 parts by weight of 2,2-dimethoxy-2-phenylacetophenone and 0.3 part by weight of 2,6-di-t-butyl-p-cresol.

[0046]

25 The composition was formed into a 1.14 mm thick photopolymer plate by means of a hot press machine at 120°C, by using a polyethylene terephthalate film support having a urethane adhesive layer and a

film having an adhesion preventing layer composed of polyvinyl alcohol and cellulose. This photopolymer plate was found to have almost no turbidity, and maintained the transparency thereof. The photopolymer plate was subjected to a 600 mJ whole area exposure from the support side by means of an exposure apparatus JET-A2-HSS (manufactured by Nihon Denshi Seiki Co., Ltd.), then the film on the opposite side was peeled off, and then a 5000 mJ image exposure was carried out through a negative film. Next, the unexposed portion was washed out by means of a flat washer (manufactured by Robo Denshi) with an aqueous developer composed of 5 parts by weight of LEOCOL SC-80 (manufactured by LION Corporation), as a surfactant, that is composed of 5-mole ethylene oxide adducts of secondary alcohols having 12 to 14 carbon atoms, 1 part by weight of dibutyldiethylene glycol as a penetrating agent, and 0.4 part by weight of sodium carbonate. The photopolymer plate was dried at 60°C for 15 minutes, and was subsequently subjected to the post-exposure by means of a chemical lamp and a sterilization lamp. The photopolymer plate was soaked for 1 minute in a 1/9 (weight ratio) ethanol/water mixed solution containing 0.1 part by weight of a methacryl-modified silicone compound X-22-174DX (manufactured by Shin-Etsu Chemical Co., Ltd.), and then dried at 60°C for 10 minutes to yield a desired photopolymer plate. The evaluation results concerned are shown in Table 1.



[0047]

[Example 2]

An objective photopolymer plate was obtained in the same manner as in Example 1 except that a  
5 methylstyryl-modified silicone compound KF-410 (manufactured by Shin-Etsu Chemical Co., Ltd.) was used in place of the methacryl-modified silicone compound X-22-174DX. The evaluation results concerned are shown in Table 1.

10 [Example 3]

A photopolymer plate obtained in the same manner as in Example 2 was used, and the photopolymer plate was further subjected to an actinic light irradiation by means of the chemical lamp and the  
15 sterilization lamp to yield a desired photopolymer plate. The evaluation results concerned are shown in Table 1.

[0048]

[Comparative Example 1]

20 The photopolymer described in Example 1 was processed through the forming, exposure and washing out steps under the same conditions as in Example 1, to yield a photopolymer plate. The photopolymer plate was dried at 60°C for 15 minutes, and then subjected to the  
25 post-exposure by means of the chemical lamp and the sterilization lamp with the same exposure light quantity to yield a predetermined photopolymer plate. The evaluation results concerned are shown in Table 1.

[0049]

[Example 4]

The photopolymer described in Example 1 was processed through the forming, exposure and washing out  
5 steps under the same conditions as in Example 1, to yield a photopolymer plate. The photopolymer plate was dried at 60°C for 15 minutes, then soaked for 1 minute in a 1% by weight ethanol solution of the methacryl-modified silicone compound X-22-164A (trade name,  
10 manufactured by Shin-Etsu Chemical Co., Ltd.), and then further dried for 5 minutes. The photopolymer plate was subjected to the post-exposure by means of the chemical lamp and the sterilization lamp to yield a desired photopolymer plate. The evaluation results  
15 concerned are shown in Table 1.

[Example 5]

An objective photopolymer plate was obtained in the same manner as in Example 4 except that a phenol-modified silicone compound X-22-1621  
20 (manufactured by Shin-Etsu Chemical Co., Ltd.) was used in place of X-22-164A. The evaluation results concerned are shown in Table 1.

[0050]

[Example 6]

25 An objective photopolymer plate was obtained in the same manner as in Example 4 except that an epoxy-modified silicone compound X-22-163A (manufactured by Shin-Etsu Chemical Co., Ltd.) was used

in place of X-22-164A. The evaluation results concerned are shown in Table 1.

[Example 7]

The photopolymer described in Example 1 was  
5 processed through the forming, exposure and washing out  
steps under the same conditions as in Example 1, to  
yield a photopolymer plate. The photopolymer plate was  
dried at 60°C for 15 minutes. Then, Asahi Guard AG5850  
(manufactured by ASAHI GLASS Co., Ltd.; a mineral  
10 spirit dilution composed of polyethylene fluoride and a  
perfluoroalkyl group-containing acrylic copolymer) was  
sprayed onto the photopolymer plate, then the  
photopolymer plate was dried at 60°C for 1 hour, and  
subjected to the post-exposure by means of the chemical  
15 lamp and the sterilization lamp to yield an objective  
photopolymer plate. The evaluation results concerned  
are shown in Table 1.

[0051]

[Example 8]

20 The photopolymer described in Example 1 was  
processed through the forming, exposure and washing out  
steps under the same conditions as in Example 1, to  
yield a photopolymer plate. The photopolymer plate was  
dried at 60°C for 15 minutes. Then, under the condition  
25 that the photopolymer plate was soaked in the 1/9  
(weight ratio) ethanol/water mixed solution in which  
0.1 part by weight of a higher fatty acid ester-  
modified silicone compound X-22-715 (trade name,

manufactured by Shin-Etsu Chemical Co., Ltd.) was dispersed, the photopolymer plate was subjected to the post-exposure by means of the chemical lamp and the sterilization lamp, to yield an objective photopolymer plate. The evaluation results concerned are shown in Table 1.

[Example 9]

An objective photopolymer plate was obtained in the same manner as in Example 8 except that a carbinol-modified silicone compound X-22-160AS (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.) was used in place of X-22-715. The evaluation results concerned are shown in Table 1.

[0052]

[Comparative Example 2]

The photopolymer described in Example 1 was processed through the forming, exposure and washing out steps under the same conditions as in Example 1, to yield a photopolymer plate. The photopolymer plate was dried at 60°C for 15 minutes. Then the photopolymer plate was soaked for 1 minute in a 1% by weight ethanol solution of a dimethylsilicone oil having no functional groups other than methyl, and then, further dried for 5 minutes. The photopolymer plate was subjected to the post-exposure by means of the chemical lamp and the sterilization lamp, to yield an objective photopolymer plate. The evaluation results concerned are shown in Table 1.

[0053]

[Example 10]

The photopolymer described in Example 1 was processed through the forming and exposure steps under the same conditions as in Example 1. Thereafter, the unexposed portion was washed out by means of the flat washer (manufactured by Robo Denshi) with an aqueous developer composed of 5 parts by weight of LEOCOL SC-80 (manufactured by LION Corporation), as a surfactant, that is composed of 5-mole ethylene oxide adducts of secondary alcohols having 12 to 14 carbon atoms, 1 part by weight of dibutyldiethylene glycol as a penetrating agent, 0.2 part by weight of a polyethylene glycol polypropylene glycol-modified silicone oil TSF4452 (manufactured by GE Toshiba Silicone Co., Ltd.) and 0.4 part by weight of sodium carbonate. The photopolymer plate was dried at 60°C for 30 minutes, and was subjected to the post-exposure by means of the chemical lamp and the sterilization lamp to yield a desired photopolymer plate. The evaluation results concerned are shown in Table 1.

[Example 11]

The photopolymer described in Example 1 was processed through the forming and exposure steps under the same conditions as in Example 1. Thereafter, an objective photopolymer plate was obtained in the same manner as in Example 10 except that the silicone compound to be added to the aqueous developer was

replaced with the carbinol-modified silicone compound X-22-160AS (manufactured by Shin-Etsu Chemical Co., Ltd.). The evaluation results concerned are shown in Table 1.

5 [0054]

[Example 12]

The photopolymer described in Example 1 was processed through the forming and exposure steps under the same conditions as in Example 1. Thereafter, an  
10 objective photopolymer plate was obtained in the same manner as in Example 10 except that the silicone compound to be added to the aqueous developer was replaced with the methacryl-modified silicone compound X-22-164A (manufactured by Shin-Etsu Chemical Co.,  
15 Ltd.). The evaluation results concerned are shown in Table 1.

[Example 13]

The photopolymer described in Example 1 was processed through the forming and exposure steps under  
20 the same conditions as in Example 1. Thereafter, an objective photopolymer plate was obtained in the same manner as in Example 10 except that the silicone compound to be added to the aqueous developer was replaced with a carboxyl-modified silicone compound X-  
25 22-162C (manufactured by Shin-Etsu Chemical Co., Ltd.). The evaluation results concerned are shown in Table 1.  
[0055]

[Example 14]

The photopolymer described in Example 1 was processed through the forming and exposure steps under the same conditions as in Example 1. Thereafter, an objective photopolymer plate was obtained in the same manner as in Example 10 except that the silicone compound to be added to the aqueous developer was replaced with an amino group-modified silicone compound KF-393 (manufactured by Shin-Etsu Chemical Co., Ltd.). The evaluation results concerned are shown in Table 1.

Table 1

Example	Hydrophobic substance	Treatment step	Actinic light irradiation after treatment
Example 1	Methacryl-modified silicone	After post-exposure	None
Example 2	Methylstyryl-modified silicone	After post-exposure	None
Example 3	Methylstyryl-modified silicone	After post-exposure	Applied
Comparative Example 1	None	-	-
Example 4	Methacryl-modified silicone	Before post-exposure	Applied
Example 5	Phenol-modified silicone	Before post-exposure	Applied
Example 6	Epoxy-modified silicone	Before post-exposure	Applied
Example 7	Acryl-modified fluorine compound	Before post-exposure	Applied
Example 8	Ester-modified silicone	During post-exposure	Applied
Example 9	Carbinol-modified silicone	During post-exposure	Applied
Comparative Example 2	Dimethylsilicone oil	Before post-exposure	Applied
Example 10	Polyether-modified silicone	During washing	Applied
Example 11	Carbinol-modified silicone	During washing	Applied
Example 12	Methacryl-modified silicone	During washing	Applied
Example 13	Carboxyl-modified silicone	During washing	Applied
Example 14	Amino-modified silicone	During washing	Applied

Continued ...



Table 1 (Cont'd)

Evaluation result							
Ink fill-in	Surface wettability (mm)	Sustainability of treatment effect		Si concentration (at%) measurement (after soaking test 1)	Evaluation in particle printing		
		Soaking test 1 (mm)	Soaking test 2 (mm)				
0	15	15	15	2.7	B		
0	15	17	18	1.9	B		
0	15	15	15	2.5	A		
13	25	Not evaluated	Not evaluated	-	C		
0	13	13	13	2.5	A		
0	16	16	Not evaluated	1.9	Not applied		
0	14	14	Not evaluated	2.2	A		
0	17	Not evaluated	Not evaluated	-	A		
0	15	16	Not evaluated	Not measured	A		
0	15	15	15	2.0	A		
11	18	23	Not evaluated	0.01	C		
0	13	13	Not evaluated	Not measured	A		
0	13	13	13	2.3	A		
0	15	15	Not evaluated	Not measured	A		
0	16	16	Not evaluated	Not measured	Not applied		
0	16	16	Not evaluated	Not measured	Not applied		

[0056]

[Comparative Referential Example 1]

A photopolymer composition was obtained by homogeneously kneading, with the kneader at 130°C, 30 parts by weight of the hydrophilic copolymer A described in the referential example, 25 parts by weight of a styrene-butadiene-styrene block copolymer (trade name: KRATON KX405, Shell Chemical), 30 parts by weight of a liquid polybutadiene (trade name: LIR305, KURARAY Co., Ltd.), 2.5 parts of hexamethylene dimethacrylate, 8 parts by weight of 2-butyl, 2-ethylpropanediol diacrylate, 2 parts by weight of 2,2-dimethoxy-2-phenylacetophenone, 0.3 part by weight of 2,6-di-t-butyl-p-cresol and 0.5 part by weight of the higher fatty acid ester-modified silicone compound X-22-715 (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0057]

The composition was formed into a 1.14 mm thick photopolymer plate by means of a hot press machine at 120°C, by using a polyethylene terephthalate film support having a urethane adhesive layer and a film having an adhesion preventing layer composed of polyvinyl alcohol and cellulose. This photopolymer plate was found to have almost no turbidity, and maintained the transparency thereof. The photopolymer plate was subjected to a 600 mJ whole area exposure from the support side by means of an exposure apparatus JET-A2-HSS (manufactured by Nihon Denshi Seiki Co.,

Ltd.), then the film on the opposite side was peeled off, and then a 5000 mJ image exposure was carried out through a negative film. Next, the unexposed portion was washed out by means of the flat washer

5 (manufactured by Robo Denshi) with an aqueous developer composed of 5 parts by weight of LEOCOL SC-80 (manufactured by LION Corporation), as a surfactant, that is composed of 5-mole ethylene oxide adducts of secondary alcohols having 12 to 14 carbon atoms, 1 part  
10 by weight of dibutyldiethylene glycol as a penetrating agent, and 0.4 part by weight of sodium carbonate. The photopolymer plate was dried at 60°C for 15 minutes, and was subsequently subjected to the post-exposure by means of a chemical lamp and a sterilization lamp to  
15 yield an objective photopolymer plate. The ink fill-in evaluation of this photopolymer plate revealed that the ink fill-in was identified in 6 halftone dots, and the result of the practical printing evaluation was graded as "C."

20 [0058]

[Comparative Referential Example 2]

The above described composition was formed into a 1.14 mm thick photopolymer plate in the same manner as in Comparative Referential Example 1 except  
25 that the amount of the higher fatty acid ester-modified silicone compound X-22-715 was altered to 2.0 parts by weight. This photopolymer plate was found to suffer turbidity; the photopolymer plate, which was subjected

to the exposure, washing and post-exposure steps in the same manner as in Comparative Referential Example 1, gave such a significantly degraded image reproducibility that void lines were blurred and  
5 halftone dots became broad in shape.

[0059]

[Example 15]

A photopolymer plate obtained by forming so as to have a thickness of 1.14 mm in the same manner as  
10 in Comparative Referential Example 1 was used. The photopolymer plate was subjected to exposure, washing and post-exposure in the same manner as in Example 12 to yield an objective photopolymer plate. The ink fill-in evaluation revealed no ink fill-in at all, and  
15 the practical printing evaluation gave the grade "A." It was found that the method of the present invention improved the performances of the photopolymer plate for which a slight amount of silicone had been internally added into the photopolymer and which had suffered  
20 slight ink fill-in and had been given no satisfactory result in the practical printing evaluation.

[0060]

[Example 16]

A commercially available water-developable  
25 solid plate AQS (manufactured by E.I du Pont de Nemours and Company) was used as a photopolymer plate. An objective photopolymer plate was obtained in the same manner as in Example 4 except that the exposure was

made by selecting the exposure light quantity for forming the image. With respect to the ink fill-in evaluation, this photopolymer plate was compared with another photopolymer plate obtained from the same AQS by subjecting the AQS to the exposure, washing and post-exposure in the same manner as in Comparative Example 1. Consequently, it was found that the treatment with a modified silicone prevented the generation of ink fill-in.

10 [0061]

[Example 17]

A commercially available water-developable solid plate Cosmolight (manufactured by TOYOBO LTD.) was used as a photopolymer plate. An objective photopolymer plate was obtained in the same manner as in Example 4 except that the exposure was made by selecting the exposure light quantity for forming the image. With respect to the ink fill-in evaluation, this photopolymer plate was compared with another photopolymer plate obtained from the same Cosmolight by subjecting the Cosmolight to the exposure, washing and post-exposure in the same manner as in Comparative Example 1. Consequently, it was found that the treatment with the modified silicone prevented the generation of ink fill-in.

[0062]

[Example 18]

A liquid photopolymer APR, F-320

(manufactured by Asahi Kasei Chemicals Corporation) was sandwiched between a cover film CF-82 (manufactured by Asahi Kasei Chemicals Corporation) and a base film BF-4B8 (manufactured by Asahi Kasei Chemicals Corporation) on an exposure apparatus ALF-213E (manufactured by Asahi Kasei Chemicals Corporation) so as to have a thickness of 2.84 mm, and the photopolymer plate thus obtained was subjected to a 150 mJ whole area exposure from the base film side. Thereafter, the photopolymer plate was subjected to a 500 mJ image exposure through a negative film, containing a solid image and halftone dots of 30, 45 and 65 lpi, disposed outside the cover film. Then, the cover film was removed and the unexposed resin was collected. Thereafter, the photopolymer plate was washed by means of a washing machine AL-400W (manufactured by Asahi Kasei Chemicals Corporation) with a washing liquid W-10 (manufactured by Asahi Kasei Chemicals Corporation). The photopolymer plate thus obtained was subjected to post-exposure in water by means of a post-exposure machine ALF-200 UP by using a chemical lamp and a sterilization lamp. Thereafter, the photopolymer plate was soaked for 10 minutes in a 1% by weight ethanol solution of an epoxy group-modified silicone compound X-22-173DX (manufactured by Shin-Etsu Chemical Co., Ltd.), and then again subjected to exposure in water by means of the post-exposure machine ALF-200UP by using the chemical lamp and the sterilization lamp, to yield an

objective photopolymer plate. From a comparison of the ink fill-in between the photopolymer plate before the treatment with the modified silicone compound and the plate subjected to the treatment with the modified  
5 silicone compound and the subsequent exposure, it was found that the treatment with the modified silicone compound prevented the generation of ink fill-in.

#### INDUSTRIAL APPLICABILITY

[0063]

10           The present invention improves the printing performances of the water-developable photopolymer plate for letterpress printing, and can be applied as a plate making method that alleviates the problems in printing.

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